

巨花雪胆中的两个新化合物*

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摘要: 从四川石棉县采集的巨花雪胆 (*Hemsleya gigantea*) 的根茎中分到 2 个新化合物, 命名为雪胆素 G 和巨花雪胆皂苷 B, 通过化学方法和波谱方法鉴定了它们的结构。另外 13 个已知化合物分别为葫芦素类和雪胆皂苷类化合物, 其中 β -香树脂醇 (3) 为首次从该属植物中得到。

关键词: 巨花雪胆; 葫芦科; 雪胆素 G; 巨花雪胆皂苷 B; 齐墩果酸苷

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A New Cucurbitacin and A New Oleanolic Acid Glycosides from *Hemsleya gigantea**

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Abstract: Two new compounds together with thirteen known compounds were isolated from the roots of *Hemsleya gigantea*. They were named Hemslecins G and Hemsiganosides B, and their structures were determined on the basis of the spectral and chemical evidences. Compound 3 was first time isolated from the genus.

Key words: *Hemsleya gigantea*; Cucurbitaceae; Hemslecins G; Hemsiganosides B.

Hemsleya gigantea is mainly distributed in southwestern part of China, especially abundant in Yunnan and Sichuan provinces. The genus plants have been used as herbal medicines in China for treatment of bronchitis, bacillary dysentery, tuberculosis, diabetes, whooping cough and bile duct infection. *Hemsleya gigantea* is a new species that comes from Sichuan province of China. Investigation on this plant led to the isolation of two new compounds, Hemslecins G (1), Hemsiganoside B (2) and thirteen known compounds, β -amyrin (3) (Cong *et al*, 2000), spinasterol (4a), 22, 23-di-

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hydro-spinasterol(**4b** ǃ Ding *et al* , 1991 ; Fan *et al* , 1988), spinasterol-3-O-β-D-glucoside(**5a**), 22 , 23-dihydro-spinasterol-3-O-β-D-glucoside(**5b** ǃ Ding *et al* , 1991 ; Fan *et al* , 1988), cucurbitacin F(**6** ǃ Yang *et al* , 1988), 23 , 24-dihydro-cucurbitacin F-25-O-acetate (**7** ǃ Yang *et al* , 2000 ; Morita *et al* , 1986), cucurbitacin F-25-O-acetate(**8**), 23 , 24-dihydro-cucurbitacin F(**9**) (Yang *et al* , 2000), 3-O-(6'-butyl ester)β-D-glucopyranosyl-oleanolic acid-28-O-α-L-arabinopyranoside(**10** ǃ Nie *et al* , 1984 ; Lin *et al* , 2003), 3-O-(6'-butyl ester)β-D-glucopyranosyl-oleanolic acid-28-O-β-D-glucopyranoside (**11** ǃ Nie *et al* , 1984 ; Lin *et al* , 2003), oleanolic acid 3-O-β-D-glucopyranoside (**12** ǃ Nie *et al* , 1984), 3-O-β-D-glucopyranosyl-oleanolic acid-28-O-α-L-arabinopyranoside (**13**), 3-O-β-D-glucopyranosyl-oleanolic acid-28-O-β-D-glucopyranoside (**14** ǃ Nie *et al* , 1984 ; Shi *et al* , 1995), 3-O-β-D-glucopyranosyl-(1→2)β-D-glucopyranosyl-oleanolic acid-28-O-β-D-glucopyranosyl-(1→6)β-D-glucopyranoside (**15** ǃ Shi *et al* , 1995).

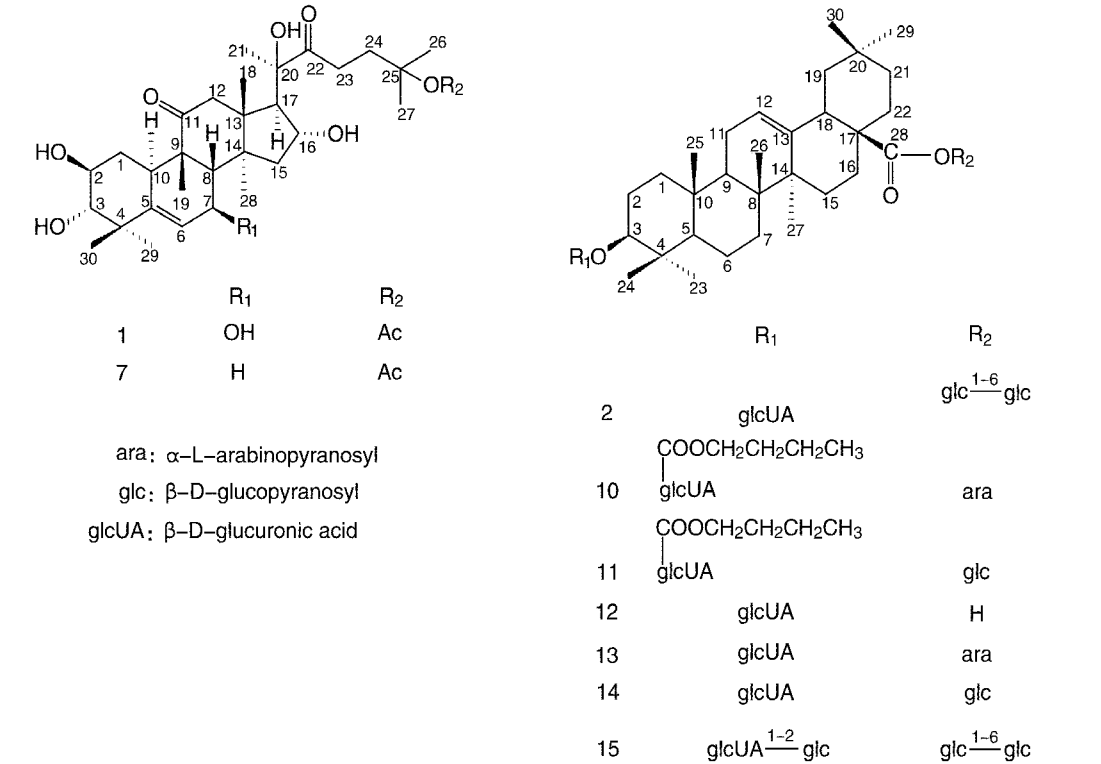


Fig. 1 Structure of compounds **1** , **2** , **7** , **10** – **15**

Hemslecins G (1) is white powder. Its molecular ion peak in negative HRFAB-MS spectrum at m/z 577.3356 ([M – H][–] , calcd. 577.3376) suggested the molecular formula of **1** was C₃₂H₅₀O₉ , which was deduced by the ¹³C NMR and DEPT. The IR spectrum showed the presence of hydroxy (3525 cm^{–1}) and acetoxy groups(1705 , 1251 cm^{–1}). The ¹³C NMR and DEPT of **1** exhibited 8 methine , 5 methylene and 9 methyl and 10 quaternary carbons , its ¹H NMR displayed 9 methyl signals

at δ_{H} 1.28, 1.33, 1.47, 1.49, 1.50, 1.58, 1.62, 1.76, 1.87 (s, $9 \times \text{CH}_3$) and olefinic proton signal at δ_{H} 6.22 (d, 1H, $J = 4.8$ Hz), these data suggested that compound **1** had the skeleton of cucurbitacin F. The ^{13}C NMR signals of **1** at δ_{C} 122.5 (CH), 1454 (C) and 215.3 (C), 217.1 (C) indicated the presence of a double olefinic carbon and two ketone group. Comparison of the ^{13}C NMR spectrum of **1** with **7**, revealed **1** had one more group. The proton of the oxymethine correlating with H-6 in $^1\text{H} - ^1\text{H}$ COSY indicated that the hydroxyl group located at C-7. The fact that the signal of C-7 in **1** was upfield shifted from δ_{C} 86.3 to δ_{C} 66.3 due to the stronger space-gauche shielding effect of the methane (C-19) with $7\beta - \text{OH}$, suggested that 7-OH was at β -orientation. Therefore, the chemical structure of compound **1** was deduced as 7β -hydroxy-23, 24-dihydrocucurbitacin F-25-O-acetate.

Hemsgiganosides B (2), white powder. On acid hydrolysis, **2** gave oleanolic acid which were identified by TLC comparison with the authentic sample. Its molecular formula of $\text{C}_{48}\text{H}_{76}\text{O}_{19}$ was determined by negative HRFAB-MS at m/z 955.4870 (calcd. 955.4902). The negative FAB-MS also displayed the peak at $[\text{M} - 1 - 162]^-$, $[\text{M} - 1 - 162 - 162]^-$ and $[\text{M} - 1 - 162 - 162 - 176]^-$, indicating that **2** contains three glucosyl units and a glucuronic acid. Comparison of the ^{13}C NMR spectrum of **2** with that of oleanolic acid, revealed that **2** had the same basic skeleton as oleanolic acid. Two carbon signals at δ_{C} 88.2, 106.0 indicated 3-linked glucuronide of oleanolic acid (Nie *et al*, 1984). By comparison of ^{13}C NMR data of **2** with that of compound **15** (Nie *et al*, 1984; Shi *et al*, 1995), it was revealed that β -D-glucopyranosyl $\{6 \rightarrow 1\}$ - β -D-glucopyranoside located at C-28 of oleanolic acid. Based on these results, the of structure of **2** was determined as 3-O- β -D-glucopyranosyl oleanolic acid 28-O- β -D-glucopyranosyl $\{1 \rightarrow 6\}$ - β -D-glucopyranoside.

The structures of compounds **3** – **15** were identified by comparing their physical and spectral data with those reported that in literatures.

Experimental

General All melting points were measured on an XRC-1 micro melting point apparatus and uncorrected. Optical rotation was taken on a SEPA-300 polarimeter. IR spectral data were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. MS spectra were recorded on a VG Auto Spec-3000 spectrometer. NMR spectra were run on a Bruker AM-400 and a DXB-500 instrument with TMS as internal standard. CC were carried out with silica gel, D101 and TLC silica gel G and silica gel GF254 (Marine Chemical Industry Factory, Qingdao). The spots were visualized by spraying with 20% H_2SO_4 followed by heating.

Plant material The sample of *Hemsleya gigantea* was collected from Shimian county of Sichuan province, China. Specimen was taxonomically identified by Wen-Jin Zhang, Pengxian County Institute for Pharmaceutical Control, Sichuan, China.

Extraction and separation The dried and powdered rhizomes of *Hemsleya gigantea* (1.9 kg) were extracted with hot methanol (65°C) for four times. The extract was evaporated to dryness *in vacuo*. This extract (653 g) was dissolved in H_2O and successively partitioned with petroleum-ester, EtOAc and *n*-BuOH to afford petroleum-ester, EtOAc and *n*-BuOH residues 13, 72, and 301 g respectively, after the solvent was evaporated *in vacuo*, The petroleum ester fraction

was repeatedly chromatographed on silica gel to give **3** (47 mg), **4a** and **4b** (75 mg), **5a** and **5b** (57 mg). The EtOAc fraction was repeatedly chromatographed on silica gel to give **1** (66 mg), **6** (715 mg), **7** (1.472 g), **8** (756 mg), **9** (3.872 g). The *n*-BuOH extract was subjected to macroporous absorption resin D-101, eluting with aq. EtOH, to give three fragments. Fractions 2–3 were further purified by repeated column chromatography on silica gel to yield **2** (0.26 mg), **10** (536 mg), **11** (589 mg), **12** (8 mg), **13** (373 mg), **14** (134 mg), **15** (1.262 g).

Compound **1**, white powder, C₃₂H₅₀O₉; mp 132–138 °C; IR ν_{max}^{KBr} cm⁻¹: 3525, 2872, 2890, 1705, 1426, 1369, 1269, 1176, 1119, 1059, 1014, 951, 870, 680; negative FAB-MS *m/z* (%): 577 [M–1][–], 560 [M–18][–]; ¹H NMR (C₅D₅N, 500 MHz) δ: 6.01 (1H, s, H–6), 4.51 (1H, m, H–7), 1.87, 1.76, 1.62, 1.58, 1.50, 1.49, 1.47, 1.33, 1.28 (27H, s, 9 × CH₃); ¹³C NMR (C₅D₅N, 125.8 MHz) see Table 1.

Table 1 ¹³C NMR data for the compounds **1** and **7**

Position	1	7	Position	1	7
1	34.7 (t)	32.9 (t)	17	59.1 (d)	57.6 (d)
2	70.5 (d)	70.1 (d)	18	22.9 (q)	21.4 (q)
3	81.3 (d)	80.4 (d)	19	15.6 (q)	18.7 (q)
4	43.0 (s)	42.0 (s)	20	80.2 (s)	79.0 (s)
5	145.3 (s)	140.7 (s)	21	25.4 (q)	24.3 (q)
6	122.5 (d)	118.8 (d)	22	217.1 (s)	214.2 (s)
7	66.3 (d)	23.5 (t)	23	32.3 (t)	30.7 (t)
8	35.5 (d)	33.6 (d)	24	35.5 (t)	34.5 (t)
9	50.4 (s)	48.3 (s)	25	81.8 (s)	81.6 (s)
10	53.2 (d)	42.5 (d)	26	26.0 (q)	25.5 (q)
11	215.2 (s)	214.0 (s)	27	26.1 (q)	25.8 (q)
12	49.5 (t)	48.6 (t)	28	19.7 (q)	19.6 (q)
13	47.9 (s)	48.1 (s)	29	20.4 (q)	19.8 (q)
14	50.4 (s)	51.0 (s)	30	25.6 (q)	24.4 (q)
15	46.6 (t)	45.2 (t)	31	170.3 (s)	170.9 (s)
16	71.0 (d)	70.4 (d)	32	22.3 (q)	22.0 (q)

(**7** in CDCl₃, **1** in C₅D₅N)

Compound **2**, white powder, C₄₈H₇₆O₁₉; IR ν_{max}^{KBr} cm⁻¹: 3415, 2938, 2848, 1699, 1606, 1429, 1386, 1160, 1024, 947; negative FAB-MS *m/z* (%): 955 [M–1][–], 793 [M–1–162][–], 631 [M–1–162–162][–], 455 [M–1–162–162–176][–]; ¹H NMR (C₅D₅N, 400 MHz) δ: 6.15 (1H, d, *J* = 8.3 Hz), 5.35 (1H, s), 4.93 (1H, t, *J* = 5.1 Hz); ¹³C NMR (C₅D₅N, 100.6 MHz) see Tables 2 and 3.

Compound **3**, white powder, C₃₀H₅₀O; mp 155–157 °C; IR ν_{max}^{KBr} cm⁻¹: 3450, 2938, 1460, 1382, 1035, 995, 659; EI-MS *m/z* (%): 426 [M]⁺, 411 [M–CH₃]⁺, 218 (100), 203, 189; ¹H NMR (CDCl₃, 500 MHz) δ: 5.16 (1H, m, H–12), 3.18 (1H, dd, *J* = 4.5 Hz, H–3α), 1.11, 0.97, 0.95, 0.91, 0.85, 0.83, 0.80, 0.77 (24H, s, 8 × CH₃) (Cong *et al.*, 2000).

Compound **4**, white needle crystals, C₂₉H₄₈O (4a), C₂₉H₅₀O (4b); mp 133–136 °C; IR ν_{max}^{KBr} cm⁻¹: 3382, 2948, 1465, 1377, 1098, 971, 938, 845, 796, 628; EI-MS *m/z* (%): 414 (100), 412 (100), 399, 397, 369, 300, 273, 271, 255, 246, 231, 147, 119, 107, (Ding *et al.*, 1991; Fan *et al.*, 1988).

Compound **5**, white needle crystals, 5a (C₃₅H₅₈O₆), 5b (C₃₅H₆₀O₆); mp 268–271 °C; EI-MS *m/z* (%): 576 [Ma]⁺, 574 [Mb]⁺, 414, 412, 397 (100), 271, 255, 83, 81; IR ν_{max}^{KBr} cm⁻¹: 3450, 2948, 1464, 1376, 1160, 1075, 1028, 971, 892, 845. (Ding *et al.*, 1991; Fan *et al.*, 1988).

Compound **6**, white gel, C₃₂H₄₈O₈; mp 98–100 °C; IR ν_{max}^{KBr} cm⁻¹: 3444, 2961, 2935, 1692, 1456, 1374, 1286, 1209, 1133, 1053, 1029, 982, 669, 612, 466; ¹H NMR (CDCl₃, 400 MHz) δ: 5.59 (1H, d, *J* = 8.4 Hz), 5.60 (1H, d, *J* = 4.3 Hz), 1.73, 1.53, 1.14, 1.08, 1.07, 0.95, 0.82, 0.79 (24H, s, 8 × CH₃).

(Yang *et al* , 1988).

Table 2 ¹³C NMR data for the aglycone moieties of compounds **2** and **10–15**

Position	2	10	11	12	13	14	15
1 (t)	37.8	38.9	37.8	38.8	38.5	38.6	38.4
2 (t)	25.6	26.7	27.2	28.4	27.7	26.2	26.5
3 (d)	88.2	89.3	88.2	89.1	90.6	88.9	89.9
4 (s)	38.5	39.6	38.5	39.5	40.2	39.3	39.2
5 (d)	54.9	55.9	54.9	55.9	57.4	55.7	56.1
6 (t)	17.5	19.3	18.3	18.6	20.1	18.4	18.2
7 (t)	32.1	33.3	33.1	33.4	34.3	33.0	33.6
8 (s)	38.9	40.0	39.0	39.8	41.0	39.8	39.3
9 (d)	47.0	48.2	47.1	48.1	48.7	47.9	47.6
10 (s)	35.9	37.1	36.0	37.1	35.7	36.8	36.2
11 (t)	22.7	23.8	22.8	23.9	24.8	23.6	23.2
12 (d)	121.8	123.0	121.9	122.6	124.6	123.0	124.0
13 (s)	143.2	144.3	143.2	144.9	145.7	144.0	144.4
14 (s)	40.7	42.2	40.8	42.1	42.2	41.6	41.3
15 (t)	25.6	28.3	29.9	28.4	27.7	26.2	26.4
16 (t)	22.4	23.9	22.5	23.9	24.8	23.3	23.5
17 (s)	45.3	47.3	46.1	46.8	49.5	46.2	46.3
18 (d)	41.2	41.8	41.2	42.3	43.7	42.0	41.7
19 (t)	46.1	46.4	45.3	46.8	47.8	46.9	46.5
20 (s)	29.7	30.9	31.6	31.1	32.4	30.7	30.2
21 (t)	33.0	34.2	32.2	34.4	34.7	33.9	33.4
22 (t)	32.1	32.8	33.1	32.2	34.3	33.0	33.4
23 (q)	27.2	28.3	27.2	29.6	29.6	28.2	28.3
24 (q)	16.0	17.0	15.9	16.7	18.6	16.9	16.6
25 (q)	14.6	15.6	14.6	15.5	17.1	15.4	15.0
26 (q)	16.5	17.6	16.5	17.5	18.9	17.4	16.2
27 (q)	25.1	26.2	25.1	26.3	25.2	26.0	25.3
28 (q , s)	175.6	176.6	175.4	181.0	178.9	177.5	176.7
29 (q)	31.5	33.3	33.1	33.4	34.3	32.4	31.8
30 (q)	22.7	23.4	22.7	23.0	25.2	23.6	22.2

(**2** , **10–15** in C₅ D₅ N)

Compound **7** , white needle crystals , C₃₂ H₅₀ O₈ ; mp 338 – 340℃ ; IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹ : 3562 , 3413 , 2974 , 1629 , 1465 , 1371 , 1280 , 1182 , 988 , 968 , 809 , 857 ; negative FAB-MS *m/z* (%) : 561 [M – 1]⁻ , 544 [M – 18]⁻ ; EI-MS *m/z* (%) : 502 , 484 , 446 , 405 , 387 , 369 , 219 , 171 , 135 , 113 , 87 ; ¹H NMR (CDCl₃ , 500 MHz) δ : 5.56 (1H , d , J = 5.6 Hz) , 3.07 (1H , d , J = 14.4 Hz) , 1.80 , 1.29 , 1.28 , 1.23 , 1.11 , 1.02 , 0.92 , 0.77 , 0.76 (27H , s , 9 × CH₃) ; ¹³C NMR (CDCl₃ , 125.8 MHz) see Table 1 (Yang *et al* , 2000 ; Morita *et al* , 1986).

Compound **8** , white powders , C₃₂ H₄₈ O₈ ; mp 218 – 220℃ ; IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹ : 3516 , 2972 , 1707 , 1691 , 1461 , 1372 , 1264 , 1126 , 990 , 971 , 932 , 845 , 622 ; EI-MS *m/z* (%) : 500 , 482 , 457 , 405 , 387 , 369 , 351 , 327 , 219 , 171 , 135 , 119 , 96 (100) , 69 ; ¹H NMR (C₅ D₅ N , 400 MHz) δ : 6.33 (1H , s) , 5.71 (1H , d , J = 6.1 Hz) , 5.09 (1H , t , J = 7.4 Hz) , 3.43 (1H , d , J = 14.4 Hz) , 1.87 , 1.68 , 1.60 , 1.55 , 1.53 , 1.46 , 1.31 , 1.22 , 1.19 (27H , s , 9 × CH₃) (Yang *et al* , 2000).

Compound **9** , white powder , C₃₀ H₄₈ O₇ ; mp 150 – 155℃ ; IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹ : 3490 , 2969 , 2886 , 1685 , 1627 , 1461 , 1373 , 1283 , 1212 , 1166 , 1056 , 1028 , 987 , 855 , 758 , 672 , 631 ; negative FAB-MS *m/z* (%) : 519 [M – 1]⁻ , 502 [M – 18]⁻ ; EI-MS *m/z* (%) : 502 , 484 , 405 , 387 , 369 , 237 , 219 , 171 , 142 , 113 , 96 , 69 ; ¹H NMR (C₅ D₅ N , 500 MHz) δ : 5.76 (1H , d , J = 5.6 Hz) , 4.39 (1H , d , J = 4.4 Hz) , 3.93 (1H , d , J = 4.4 Hz) , 1.42 , 1.39 , 1.34 , 1.21 , 1.19 , 1.08 , 1.02 , 0.95 (24H , s , 8 × CH₃) (Yang *et al* , 2000).

Compound **10**, white powder, $C_{45}H_{72}O_{13}$; IR ν_{\max}^{KBr} cm^{-1} : 3490, 2940, 1730, 1388, 1364, 1259, 1163, 1027, 950, 826, 776, 749, 631, 599; negative FAB-MS m/z (%): 819[$M - 1$]⁻, 763[$M - 1 - 56$]⁻, 687[$M - 1 - 132$]⁻ (100), 455[$M - 1 - 132 - 176 - 56$]⁻; ^1H NMR (C_5D_5N , 400 MHz) δ : 6.26 (1H, d, $J = 5.8$ Hz, ara H - 1), 4.97 (1H, d, $J = 7.7$ Hz, glcUA H - 1), 1.31, 1.29, 1.14, 1.12, 0.99, 0.94, 0.88 (21H, s, $7 \times \text{CH}_3$), 0.74 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (C_5D_5N , 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Lin *et al*, 2003).

Table 3 ^{13}C NMR data for the sugar moieties of **2** and **10–15**

	Position	2	10	11	12	13	14	15
3-O-glcUA	1	106.0	107.3	106.3	106.7	107.9	107.0	105.6
	2	77.2	75.5	76.3	75.3	76.7	76.6	78.7
	3	76.6	78.1	77.9	78.1	77.7	75.1	78.0
	4	72.8	73.1	73.2	73.8	72.8	73.9	71.7
	5	77.6	77.4	77.0	77.0	79.5	78.1	76.7
	6	171.6	170.34	169.3	176.9	178.0	176.3	176.3
COOCH ₂ CH ₂ CH ₂ CH ₃	α		65.0	61.3				
	β		30.0	29.8				
	γ		18.6	17.5				
	δ		13.8	12.7				
glc' (1→2)	1							105.2
	2							78.0
	3							78.7
	4							71.7
	5							78.0
	6							63.0
ara (1→3)	1							
	2							
	3							
	4							
	5							
28-O-ara	1		95.7			97.3		
	2		71.4			69.5		
	3		73.9			75.4		
	4		66.0			75.0		
	5		66.1			67.6		
28-O-glc	1	94.6		94.8			95.6	95.8
	2	74.4		74.4			74.0	74.0
	3	76.6		72.0			78.8	75.2
	4	70.9		70.3			71.1	71.0
	5	77.2		78.2			79.1	78.4
	6	68.4		63.9			62.2	69.6
glc' (1→6)	1	104.0						105.2
	2	77.0						73.6
	3	76.2						78.4
	4	70.5						71.1
	5	77.1						78.7
	6	61.1						62.8

Compound **11**, white powder, $C_{46}H_{74}O_{14}$; IR ν_{\max}^{KBr} cm^{-1} : 3401, 2925, 2859, 1737, 1461, 1372, 1162, 1070, 627; negative FAB-MS m/z (%): 849[$M - 1$]⁻, 793[$M - 1 - 56$]⁻ (7), 687[$M - 1 - 162$]⁻ (100), 455[$M - 1 - 162 - 176 - 56$]⁻ (21); ^1H NMR (C_5D_5N , 400 MHz) δ : 6.31 (1H, d, $J = 8.0$ Hz, glc H - 1), 4.99 (1H, d, $J = 7.7$ Hz, glcUA H - 1), 1.27, 1.25, 1.07, 0.95, 0.90, 0.87, 0.82 (21H, s, $7 \times \text{CH}_3$), 0.75 (3H, t, $J = 7.3$ Hz); ^{13}C NMR (C_5D_5N , 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Lin *et al*, 2003).

Compound **12**, white powder, $C_{36}H_{56}O_9$; [α]_D^{25.3} + 8.35°C (c 0.479, C_5D_5N); IR ν_{\max}^{KBr} cm^{-1} : 3950, 2934,

2863, 1692, 1610, 1458, 1436, 1386, 1274, 1208, 1161, 1078, 1029, 982, 948, 635; negative FAB-MS m/z (%): 631 (100) [M - 1]⁻, 455 [M - 1 - 176]⁻; EI-MS m/z (%): 456, 412, 248 (100), 203, 163; ¹H NMR (C₅D₅N, 400 MHz) δ : 5.68 (1H, m, H - 12), 5.60 (1H, m, glcUA H - 1); ¹³C NMR (C₅D₅N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984).

Compound **13**, white needle crystals, C₄₁H₆₄O₁₃; IR ν_{\max}^{KBr} cm⁻¹: 3434, 2940, 2836, 1741, 1595, 1463, 1388, 1160, 1075, 776; negative FAB-MS m/z (%): 763 [M - 1]⁻, 631 [M - 1 - 132]⁻, 455 [M - 1 - 132 - 176]⁻; ¹H NMR (C₅D₅N, 400 MHz) δ : 6.24 (1H, d, J = 5.2 Hz), 5.41 (1H, m, H - 12); ¹³C NMR (C₅D₅N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Shi *et al*, 1995).

Compound **14**, white needle crystals, C₄₂H₆₆O₁₄; IR ν_{\max}^{KBr} cm⁻¹: 3415, 2938, 2848, 1699, 1606, 1429, 1386, 1160, 1024, 947; negative FAB-MS m/z (%): 794 [M - H]⁻, 631 [M - 1 - 162]⁻, 455 [M - 1 - 162 - 176]⁻; EI-MS m/z (%): 456, 410, 392, 248, 203, 163; ¹H NMR (C₅D₅N, 400 MHz) δ : 6.32 (1H, d, J = 7.7 Hz, glc H - 1), 5.41 (1H, s, H - 12), 5.17 (1H, m, glcUA H - 1); ¹³C NMR (C₅D₅N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Shi *et al*, 1995).

Compound **15**, white powder, C₅₄H₈₆O₂₄; negative FAB-MS m/z (%): 1117 [M - 1]⁻, 955 [M - 1 - 162]⁻, 793 [M - 1 - 162 - 162]⁻, 631 [M - 1 - 162 - 162 - 162]⁻, 455 [M - 1 - 162 - 162 - 162 - 176]⁻; ¹H NMR (C₅D₅N, 400 MHz) δ : 6.44 (1H, d, J = 8.8 Hz), 6.2 (1H, m), 5.91 (1H, m); ¹³C NMR (C₅D₅N, 100.6 MHz) see Tables 2 and 3 (Shi *et al*, 1995).

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